Microtubular solid oxide fuel cells with lanthanum strontium manganite infiltrated cathodes

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Abstract

Microtubular solid oxide fuel cells (mT-SOFCs) with infiltrated cathodes were fabricated and their electrochemical performance were compared with standard cells. For this purpose, NiO-YSZ (yttria stabilized zirconia) microtubular supports were fabricated by cold isostatic pressing (CIP) of NiO, YSZ and pore former powders, followed by spray coating of the YSZ electrolyte and co-sintering at 1400 ºC. The LSM ($La_{0.8}Sr_{0.2}MnO_{3-\delta}$)-YSZ oxygen electrode is deposited by infiltration of LSM (into a thin porous YSZ layer). One of the advantages of this fabrication method is an increase of TPB (triple-phase boundary) length compared with the standard LSM-YSZ composite due to the much finer dispersed LSM particles having a higher active surface area towards oxygen reduction.

The effect of the infiltrated amount in cell performance was studied. Two cells with identical anode support and thin layer electrolyte and 22 vol.% (cell A) and 35 vol.% (cell B) infiltrated LSM were prepared. The infiltrated cells showed an increase of up to 50% in terms of power density compared to the standard cell (550 mW cm^{-2} at 0.7 V and 850 ºC for a standard cell having 50 vol.% LSM and 720 and 805 mW cm^{-2} at 0.7 V and 850 ºC for infiltrated cells A and B, respectively). The results indicate that the infiltrated cathode with fine distributed LSM particles improve the fuel cell

performance using a lower LSM content compared with standard LSM-YSZ composite cathodes.

1. Introduction

Microtubular solid oxide fuel cells (mT-SOFC) have recently attracted much interest for both fuel cells and electrolysis applications, as they are more resistant to thermal cycling, and they present shorter start-up/shut-down times and higher volumetric power densities in comparison with the traditional planar geometry.[1,2,3,4]

The most preferred configuration for mT-SOFCs is that of standard NiO-YSZ (yttria stabilized zirconia) anode supports typically fabricated by extrusion,[5,6] cold isostatic pressing (CIP),[7] gelcasting,[8] subsequent dip coating,[9] slip casting[10,11] or by the immersion induced inversion method.[12] Deposition of the electrolyte materials is usually performed by spray coating[3] or dipcoating[3] followed by co-sintering at temperatures in the range of 1350-1500 ºC. Alternatively to sintering processes, infiltration of catalyst nanoparticles into a ceramic porous matrix has been successfully proposed for electrode fabrication in SOFCs, as extensively summarized in several review articles.[13,14,15,16 17,18] Fabrication of electrodes by infiltration may contribute to reducing some problems found in standard fabrication methods, as a cathode sintering stage is no longer necessary. For example, in the case of LSM infiltration, formation of non-conducting secondary phases such as zirconates ($La_2Zr_2O_7$, $SrZrO_3$) is avoided due to the much lower firing temperature (600 ºC vs 1150 ºC). Moreover, infiltration of the catalyst in the YSZ porous backbone minimizes the thermal expansion mismatch between the YSZ electrolyte and the cathode, reducing the risk of electrode cracking. In fact, electrode delamination is a serious concern during mT-SOFC fabrication that increases the resistance of the cell. Another advantage is an increased TPB (triple-phase boundary) length compared with standard cathodes due to the smaller size of the dispersed catalyst particles. In the case of infiltration, the lower firing temperature inhibits the coarsening of the catalyst during the sintering process. However, the main

drawback of the infiltration method is to attain enough density of electrode material to allow for good electrical conductivity in the cathode. In order to introduce sufficient amount of catalyst and reduce the electrode resistance, several infiltration steps might be required increasing fabrication costs.[19]

For example, $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) cathode, presenting excellent surface oxygen exchange rate, electrical conductivity and bulk oxygen ion diffusion coefficient, it was recently reported by impregnation into a porous $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)-gadolinia-doped ceria (GDC) composite backbone. The resulting cell showed similar current density values (~2 A cm^{-2}) under both SOFC (0.7 V) and solid oxide electrolysis cell (SOEC) (1.2 V) operating conditions.[20]

It is also well-known that nickelates react with YSZ at the sintering temperatures, and this reactivity could be avoided by infiltration of the salt precursors to form the nickelate phase. It was recently reported by the authors that anode supported microtubular cells with a cathode composed of $Nd_2NiO_{4+\delta}$ infiltrated into porous yttria stabilized zirconia (YSZ), showed maximum power densities of 0.4 W cm^{-2} at 600 ºC using a thin YSZ layer as the electrolyte. In addition no degradation was detected after 24 hours under current load.[21] Finally, La_2NiO_4 electrodes, using $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) or $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) as the porous matrix, were successfully fabricated by an infiltration method. The cells were tested at 650 °C for 210 h under 150 mA cm^{-2} showing no degradation.[22]

Improvement in the cell performance upon LSM infiltration into a porous YSZ scaffold compared to the traditional composite LSM-YSZ cathode has been previously reported, and associated to enhanced triple phase boundary (TPB) length and catalytic activity.[23]

This manuscript extends to cells produced by a different method and study the effect of LSM ($La_{0.8}Sr_{0.2}MnO_{3-\delta}$) infiltration loading on the electrochemical performance.

2. Experimental

NiO-YSZ tubes were fabricated by cold isostatic pressing (CIP) as described in references [7,24,25]. A YSZ electrolyte was subsequently deposited by wet powder spraying (WPS) using a suspension of YSZ powder (TZ-8Y, Tosoh, 99.9%). After drying, the cells were co-sintered at 1400 °C for 2 hours. Typical dimensions of the half-cells are 100 mm length, ~350 µm wall thickness, and 2.4 mm inner diameter. The YSZ electrolyte thicknes is ~15 µm.

To coat a thin porous layer (TPL) for cathode infiltration, YSZ (calcined at 1500 °C, milled for 72 h in water and dried) was mixed with 20 vol.% graphite (Sigma Aldrich <325 mesh), azeotropic solvent (toluene/ethanol), dispersant (100 g Menhaden fish oil dissolved in 1 L of aezotropic solvent), and binder (200 g polyvinyl butyral dissolved in 1 litre of aezotropic solvent). Additional details are explained in references [19,22,26]. The sintered thin porous layer was then infiltrated with a LSM ($La_{0.8}Sr_{0.2}MnO_{3-\delta}$) cathode using nitrate precursors. Phase purity of the LSM phase was confirmed by XRD. The details of the infiltration process and recipe used are addressed in the same references. Two different cell types were prepared for the present study, where anode and electrolyte are identical for both cells. The difference between cells is the amount of LSM infiltrated. The cells with two times and four times LSM infiltrated cathodes are called cell A (22 vol.% of LSM) and cell B (35 vol.% of LSM), respectively.

Electrochemical characterization was performed using the experimental setup described in reference [27]. Electrical contacts were made using platinum wire in a four probe setup configuration. Ni mesh was used as current collector in the anode side. Cathode current collection was performed by coiling the Pt wire around the LSM-YSZ cathode and adding Pt paste to improve electrical contact. The cells were then sealed to alumina tubes using a ceramic sealant (Aremco, Ceramabond 503) and heated up to 800 ºC under a nitrogen atmosphere, whereas the cathode side was exposed to ambient air. Subsequently, nitrogen gas was switched to pure humidified hydrogen, reducing NiO to metallic Ni at the anode. *j*-V (current density-voltage) curves were recorded in galvanodynamic mode using a scan rate of 2.5 mA cm^{-2} s^{-1} and EIS (electrochemical impedance spectroscopy) measurements were performed under OCV (open circuit voltage) conditions using 20 mV of sinusoidal amplitude and a frequency range from 100 kHz to 100 mHz. These experiments were performed using a VSP potentiostat/galvanostat (Princeton Applied Research, Oak Ridge, USA).

Microstructural characterization of fractured samples was performed using a JEOL 6301F scanning electron microscope (SEM).

3. Results and discussion

3.1. Infiltration studies and microstructure

In electrode fabrication there is always a trade-off between permeation for gases, related with material porosity, and the electrical conductivity associated with percolation of the conductive phase, LSM for the present study. Both, permeation and electrical conduction should be as high as possible. In the present work, the cathodes are fabricated by impregnation of a porous YSZ layer with LSM, containing an initial pore

volume ~~of the porous YSZ~~ of about 50%. Impregnation with LSM will result in a decrease of porosity.

In order to get an insight into the dependence of the cell performance as a function of the impregnated volume, two identical cells using different LSM loads were prepared. The two cells, A and B, show about 22 vol.% and 35 vol.% infiltrated LSM in the fabricated cathode, respectively. This amount of infiltration for cell A and cell B leads to 14% and 27% porosity reduction, respectively, from the original 50% open porosity prior to infiltration leaving sufficient porosity for gas diffusion. The details of calculating the amount of infiltrate and porosity change upon infiltration are summarized in reference [21]. Note that the cathode in standard cells, typically fabricated by techniques such as by dip-coating, generally are composed of 50/50 vol.% LSM, with 37% of pores.[25]

The microstructure of the infiltrated cells is shown in figure 1. In cell A, the Ni-YSZ porous support (~400 µm thick) provides the mechanical integrity for the cell. The interfaces between the cathode, electrolyte and part of the cell anode are shown in Figure 1(a). SEM micrographs show high quality interfaces between the component layers. A root-tree-type interface is produced in the anode side. As for the cathode, the good adhesion is caused by the YSZ scaffold fabrication procedure, as high temperature sintering was performed. The cathode and electrolyte thickness are ~40 µm and ~15 µm, respectively. LSM shows excellent distribution of connected fine particles (50-100 nm) on YSZ where they meet the electrolyte (Figure 1(b)). The distribution of LSM particles within the cathode are expected to provide high catalytic activity favouring the electrochemical reactions and a continuous current path. In cell B, the anode support, electrolyte and cathode thicknesses are in the same range: ~400, ~15 and ~40 µm,

respectively. Figure 1(c) shows the excellent quality of the interfaces in this cell. The fine infiltrated LSM particles (~100 nm), again show homogeneous distribution and also connectivity within the cathode microstructure (Figure 1d and e). YSZ particles are well covered with these nano sized LSM particles but also leaving well connected pores. High values in the TPB length are expected for this microstructure.

3.2. Electrochemical characterization

Characteristic current density-voltage (*j*-*V*) and power density-voltage (*P*-*V*) curves from 700-850 ºC are shown in figure 2 for both cells A and B. Values of a standard Ni-YSZ/YSZ/LSM-YSZ microtubular cell of similar dimensions are also shown for comparison. Electrochemical performance for both cells is significantly enhanced, as compared with that of the standard cell. The effect is more noticeable at lower temperatures (see table 1). For example, at 850 ºC, measured power densities at 0.7 V are about 720 and 805 mW cm^{-2} for cell A and cell B, respectively, and 550 mW cm^{-2} for ~~an~~ the standard cell. At 800 ºC, the values are 615, 700 and 370 mW cm^{-2}, for cells A, B and the standard cell, respectively. This effect might be due to the low catalytic activity of LSM at temperatures below 800 ºC, which is partially compensated by the finest particle size in the case of the impregnated cathodes. Interestingly, the performance of infiltrated electrodes exhibited an almost temperature independent increase of about 10% in terms of output power, with increasing content of LSM.

From our knowledge, these results point out the best performance reported to date for microtubular cells using conventional materials: Ni-YSZ for the anode, YSZ as the electrolyte and LSM-YSZ for the cathode. The reason for this significant enhancement is the suitable dispersion of LSM nanoparticles within the cathode, which might

enhance the TPB length at the same time that assure good pore and electrical connectivity. Similar improvements were previously reported for LSM infiltrated cathodes in planar SOFCs, as for example demonstrated by Armstrong and Virkar,[28] and also by Sholklapper *et al*.[29]

In addition, short-term durability studies of 24 hours under constant operation at 800 ºC and 0.7 V showed no degradation for both cells A and B. In fact, there was a 3.4% and 2.1% increase, for cell A and B, respectively, which was attributed to reorganization of nickel particles in the Ni-YSZ anode support. Apparently, and based on a careful examination of SEM images, no microstructural changes were observed before and after cell testing, and the LSM nanoparticles at the cathode remain unaltered (after 24 hours under current load at 800 ºC) confirming the stability of the cathode. Long-term durability experiments are under study.

3.2. Electrochemical impedance spectroscopy measurements

Electrochemical impedance spectroscopy (EIS) was also performed under OCV conditions, in order to analyze the different limiting steps contributing to the cell polarization. The different EIS spectra for the studied temperature range are shown in figure 3. All data were fitted using an equivalent circuit consisting of the following elements: an inductance (L), an ohmic resistance (R_{ohm}), two resistance-constant phase elements (R_1CPE1, R_3CPE3), and one finite length Warburg diffusion element (W_2). A summary of the fitting parameters for the EIS data is shown in Table 2. It can be observed that the ohmic resistance values are the same, between the error limits, for both cells. These resistance values are consistent with those expected for a thin YSZ electrolyte (~15 µm), assuring good electrical connections and no losses associated with

lateral current conduction through the cathodes. The R_2 contribution, fitted with the finite length Warburg element (W_2), is nearly constant with temperature, and also almost identical for both cells. This component of the EIS data was assigned to gas diffusion through the anode support of the cells. The R_2 values were also consistent with cells with the same anodic support.[21] On the contrary, R_1 was found to be thermally activated and, in general, rather similar, at least at the higher temperatures, when comparing cells A and B. As a consequence, this contribution was assigned to charge transfer at the Ni-YSZ anode, also consistent with previous results.[7,21] Finally, the last contribution (R_3) was assigned to charge transfer at the LSM-YSZ cathode, as this component is also thermally activated. The values are significantly lower for cell B in comparison with cell A, due to the increased number of LSM particles.

4. Conclusions

Infiltration of LSM particles into porous YSZ skeletons is shown as an adequate technique to fabricate SOFC cathodes for microtubular cells. The performance of two similar cells using different LSM infiltrated loads was compared. At temperatures between 700 and 800ºC the cell with a 22 vol.% LSM cathode shows an improvement in power output as compared with that of standard mT-SOFC cell of about 65%. A cell with 35 vol.% of LSM charge presents an improvement of about 80%. The improvement is due to the homogeneous distribution of very fine LSM particles in the YSZ porous scaffold producing a very efficient and well-integrated cathode.

There is still open the question of the optimum LSM infiltrate loading. According to our results, good electrochemical performance as that of cell A is obtained with relatively low LSM content, half of that of standard cells.

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FIGURE CAPTIONS

Figure 1. SEM images showing (a) the interface between anode, electrolyte and cathode in cell A, (b) LSM distribution in the cathode of cell A, (c) the interface of the anode. electrolyte and the cathode in cell B, (d) and (e) LSM distribution in the cathode of cell B.

Figure 2. Electrochemical performance (current and power density vs. voltage) at 700 – 850 ºC for cell A (a) and cell B (b) and the standard cell (a and b).

Figure 3. EIS spectra recorded as a function of temperature for cell A (a) and cell B (b).

Table 1. Summary of the electrochemical properties for both cell A and cell B, as well as for a standard cell

Cell	**Temp (°C)**	**OCV (V)**	***j* at 0.7 V (mA cm^{-2})**	***P* at 0.7 V (mW cm^{-2})**	**% increase** **(vs. standard cell)**
A	700	1.10	330	230	64
A	750	1.09	555	390	66
A	800	1.08	875	615	66
A	850	1.07	1030	720	30
B	700	1.10	350	245	75
B	750	1.09	600	420	78
B	800	1.08	995	700	89
B	850	1.07	1150	805	46
Standard	700	1.10	200	140	-
Standard	750	1.09	335	235	-
Standard	800	1.07	525	370	-
Standard	850	1.06	790	550	-

Table 2. Summary of the fitting parameters from EIS data for cells A and B. The fitting error is shown in brackets.

Cell	Temp (°C)	R_{ohm} (Ωcm^2)	R_1 (Ωcm^2)	R_2 (Ωcm^2)	R_3 (Ωcm^2)	ASR (Ωcm^2)
A	700	0.17(1)	0.18(1)	0.23(1)	0,80(1)	1.38(4)
A	750	0.12(1)	0.12(1)	0.21(4)	0,66(1)	1.10(7)
A	800	0.10(1)	0.07(1)	0.20(2)	0.38(1)	0.75(5)
A	850	0.09(1)	0.05(1)	0.18(3)	0.36(1)	0.69(6)
B	700	0.15(2)	0.30(5)	0.17(1)	0.58(5)	1.19(9)
B	750	0.11(5)	0.03(1)	0.17(2)	0.45(4)	0.76(8)
B	800	0.10(7)	0.06(1)	0.20(1)	0.21(1)	0.58(5)
B	850	0.09(1)	0.07(1)	0.18(1)	0.17(3)	0.51(3)

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